CMAS Interactions with Advanced Environmental Barrier Coatings Deposited via Plasma Spray-Physical Vapor Deposition

B. J. Harder, V. L. Wiesner, and D. Zhu

NASA Glenn Research Center, Cleveland OH 44135

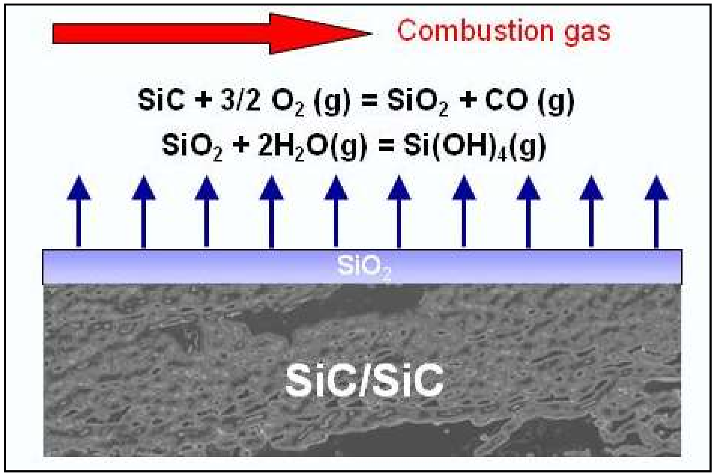
N. S. Johnson

Colorado School of Mines, Golden CO 80401

Work supported by the Transformative Tools and Technologies (TTT) Project as part of the Transformative Aeronautics Concepts (TACP) Program

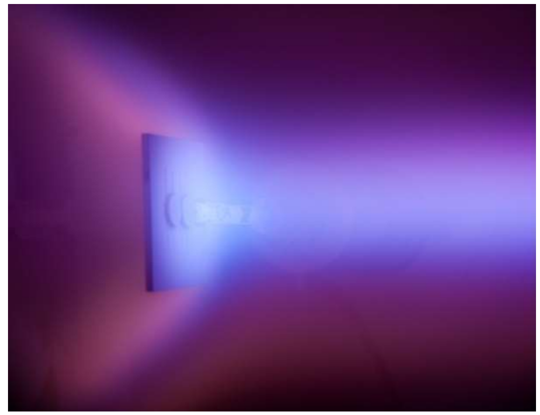
Motivation

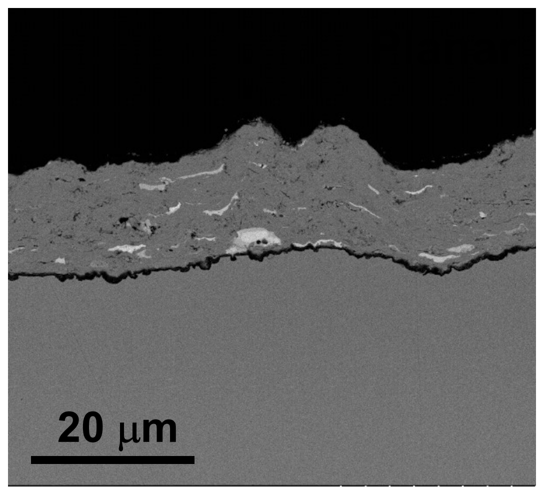
- Incorporation of Si-based ceramics into turbine hot section has substantial benefits
  - Limited by water vapor attack
- Environmental barrier coatings (EBCs) are necessary to protect the underlying ceramic
- Current NASA goals require durable coating systems at 1482C (2700F)
  - Limited recession and good adhesion
- Traditional processing methods may not be able to meet the requirements
  - Plasma Spray-Physical Vapor Deposition (PS-PVD)

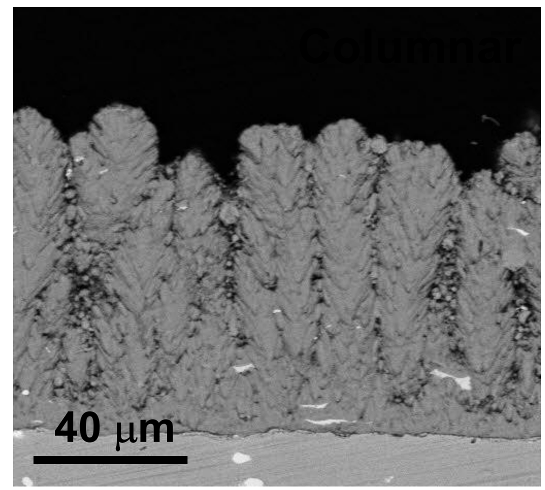


Plasma Spray-Physical Vapor Deposition (PS-PVD)

- Bridges the gap between plasma spray and vapor phase methods
  - Variable microstructure
  - Multilayer coatings with a single deposition
- Low pressure (70-1400 Pa)
  High power (>100 kW)
  - Temperatures 6,000-10,000K
- High throughput[1]
  - 0.5 m^2 area, 10 μm layer in < 60s
- Material incorporated into gas stream
  - Non line-of-sight deposition
- Attractive for a range of applications
  - Solid oxide fuel cells, gas sensors, etc.







[1]A. Refke, et al. *Proceedings of the International Thermal Spray Conference, May 14-18,* (Beijing, China), 705-10 (2007).

$Yb_2Si_2O_7$/Si-HfO_2 EBCs

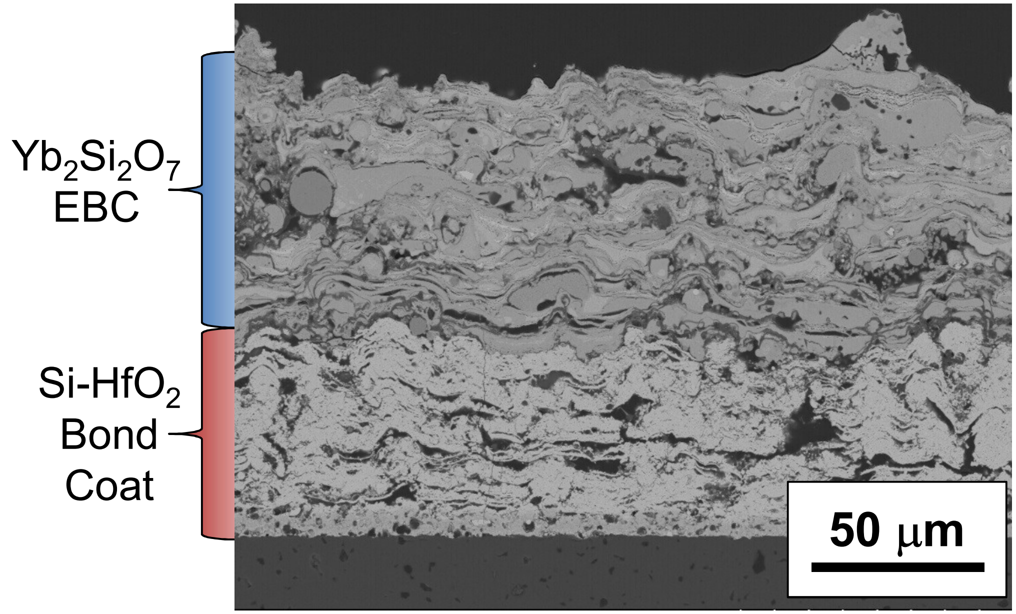
- Bulk SiC substrates 0.5” x 0.75”

- Bond coat was Si-HfO_2
  - “Bricks and Mortar” structure
  - Starting powder 30/70 mol% HfO_2/Si

- SiO_2-lean Yb-silicate
  - 35 mol% Yb_2O_3 bal SiO_2
  - Fully reacted 85/15 wt% $Yb_2Si_2O_7$/Yb_2SiO_5
  - After deposition coating contained some free SiO_2 (~10 wt%)

- Heated in air to 1300°C for 20hr prior to CMAS exposure

As-deposited 2-layer EBC

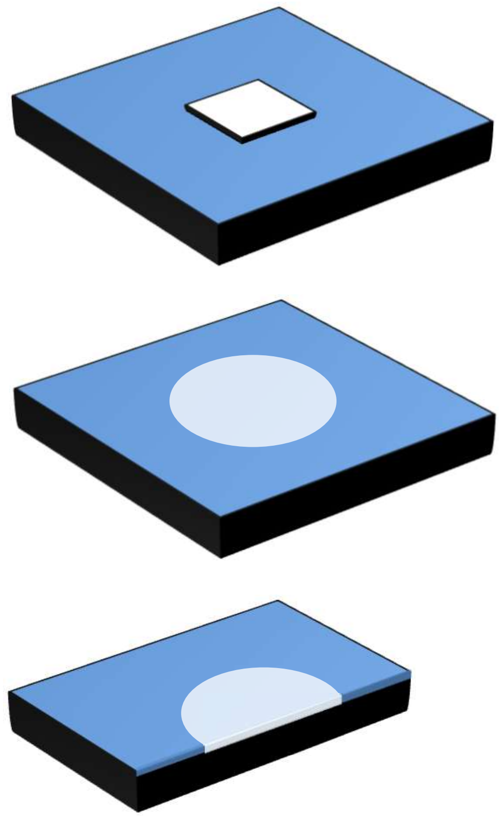


CMAS Exposure

- CMAS composition was melted at 1500°C and quenched
- CMAS was milled and tape cast at a loading of ~29 mg/cm^2
- Tape area for exposure ~ 2mm x 2mm
  - Total tape weight before burnout 1.50 - 2.0 mg
- Binder burnout at 500°C (6 hr)
- Ramp rate ~5°C/min to target temp
- Cross-section through center of reacted zone

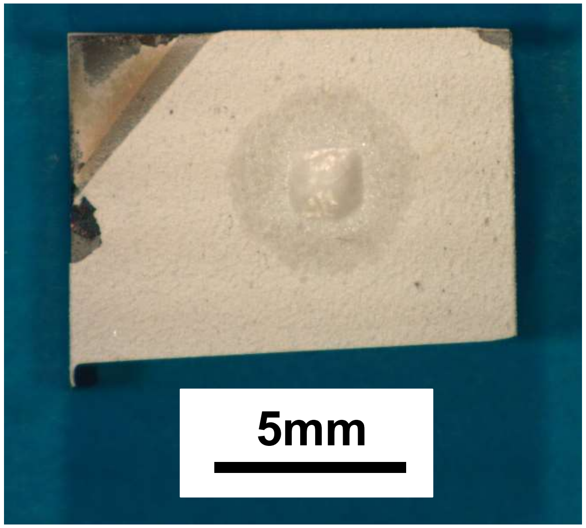
CMAS Composition (mol%)

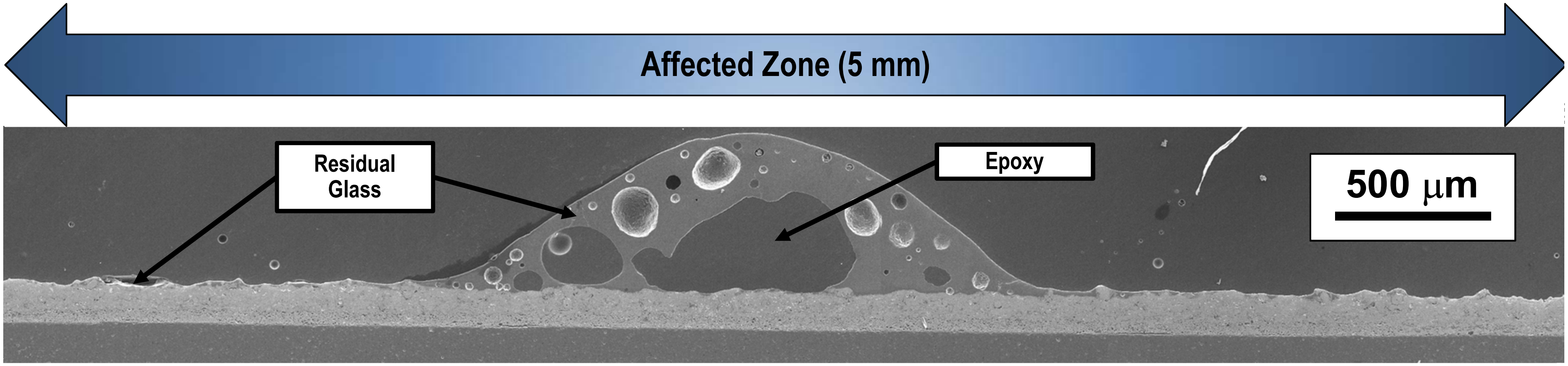
CaO	MgO	Al_2O_3	SiO_2	Na_2O	K_2O	Fe_2O_3
23.3	6.4	3.1	62.5	4.1	0.5	0.05



1200°C/10hr

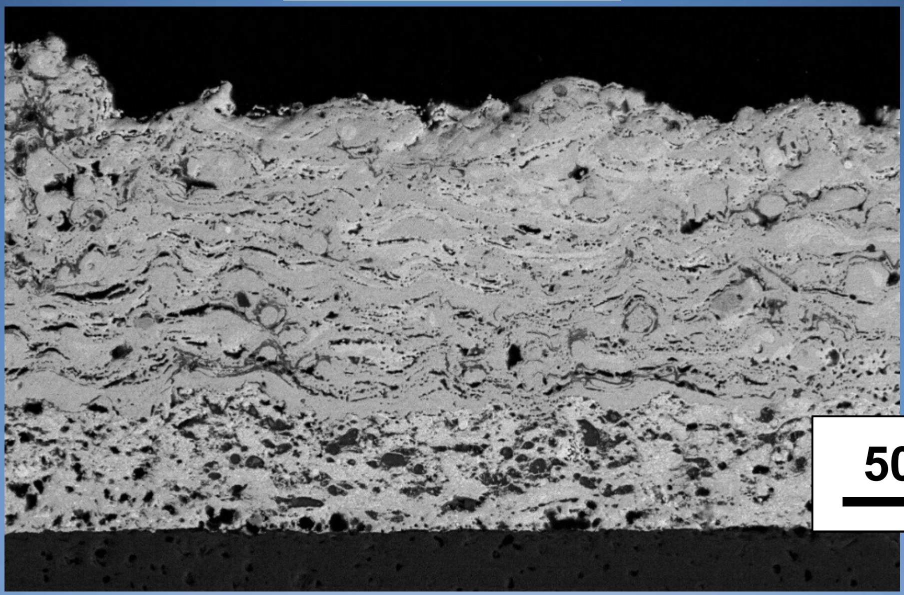
- Tape became shiny and exhibited wetting on the surface of the coating
- Total 'affected zone' was ~5mm
- Macro image showed the glass did not go fully molten



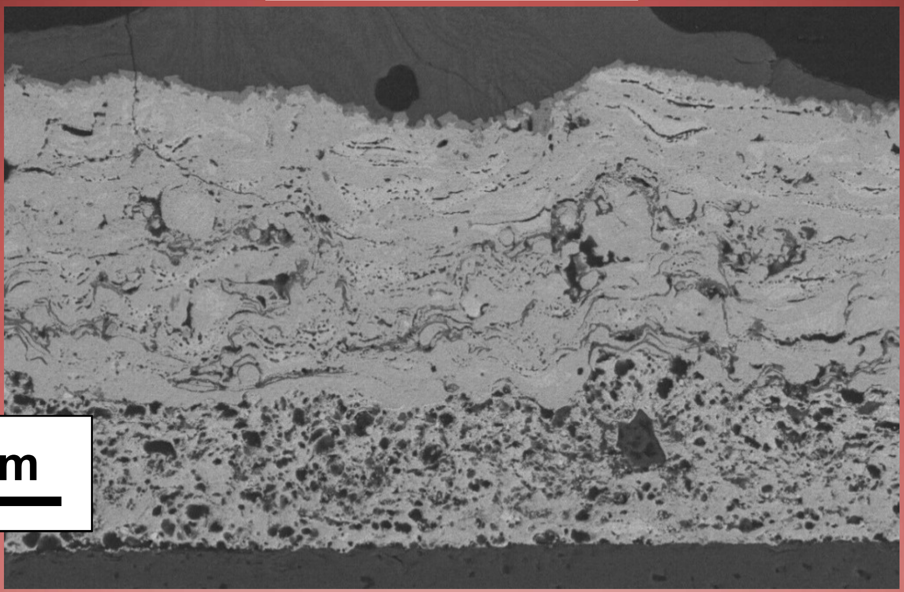


1200°C/10hr

Unreacted



With CMAS

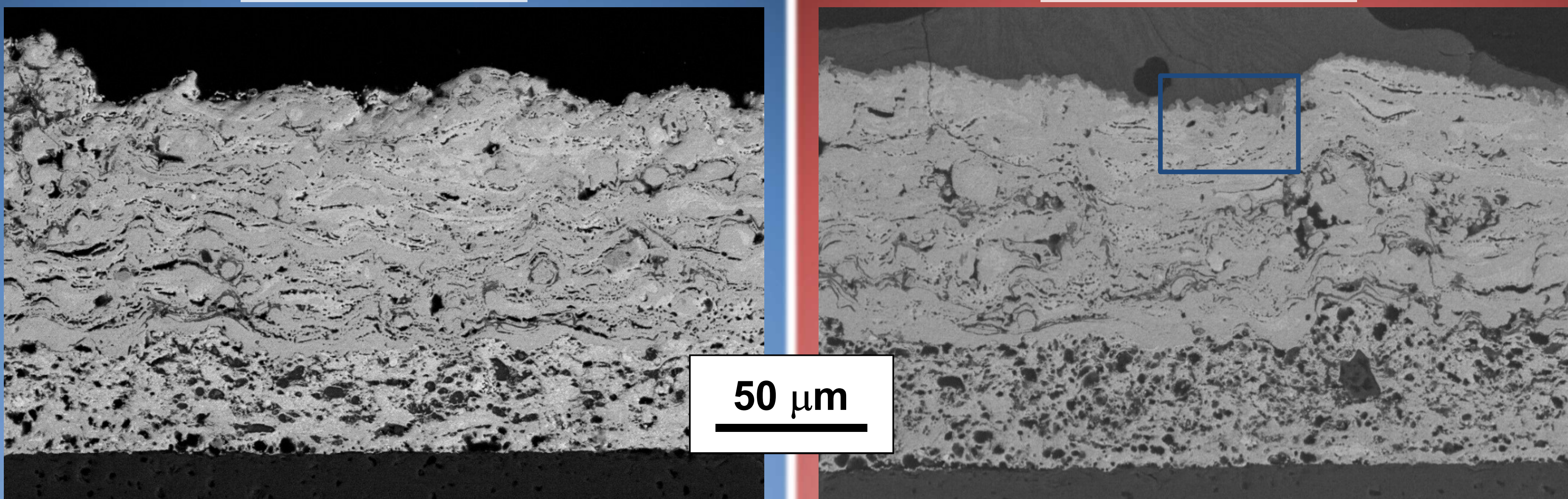


- Glass did not significantly attack or infiltrate the EBC
- Interaction zone with top of EBC layer of ~10μm
  - Si:Ca:Yb ratio of 3:1:1
- Underlying EBC and bond coat did not show any signs of glass infiltration

1200°C/10hr

Unreacted

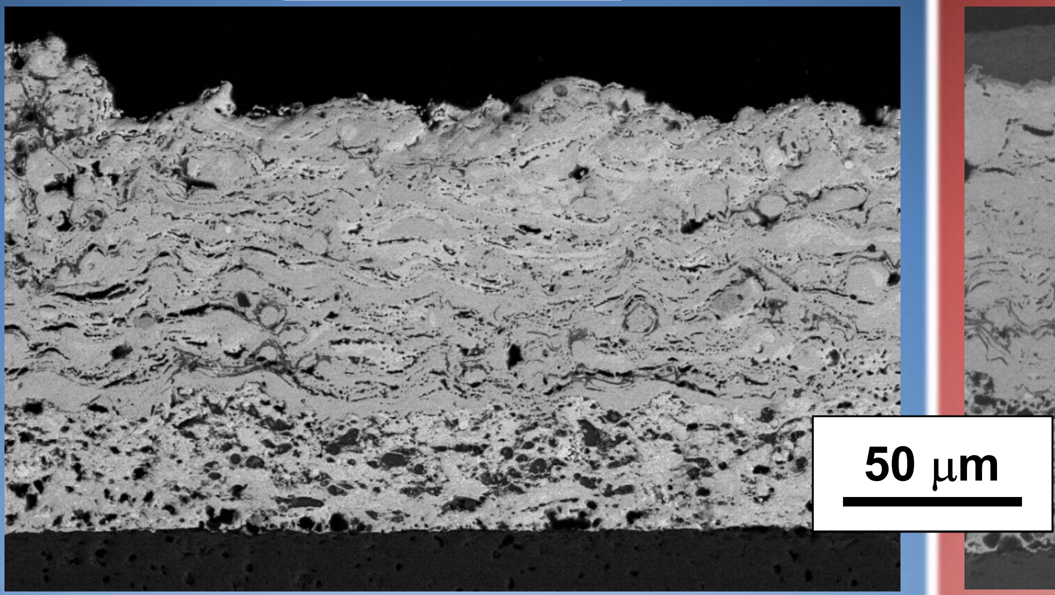
With CMAS



- Glass did not significantly attack or infiltrate the EBC
- Interaction zone with top of EBC layer of ~10μm
  - Si:Ca:Yb ratio of 3:1:1
- Underlying EBC and bond coat did not show any signs of glass infiltration

1200°C/10hr

Unreacted

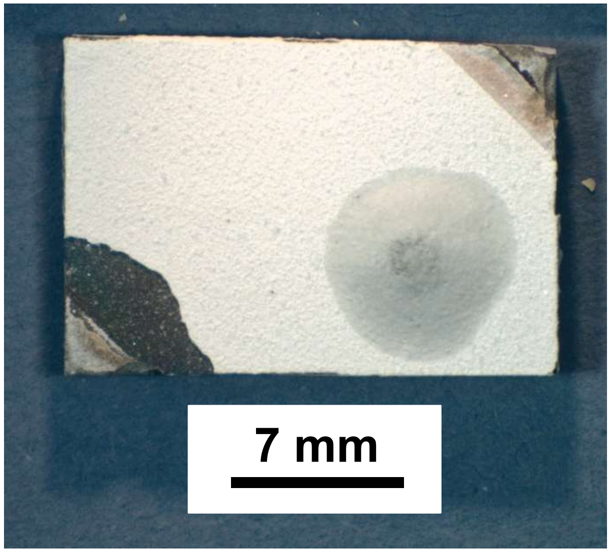


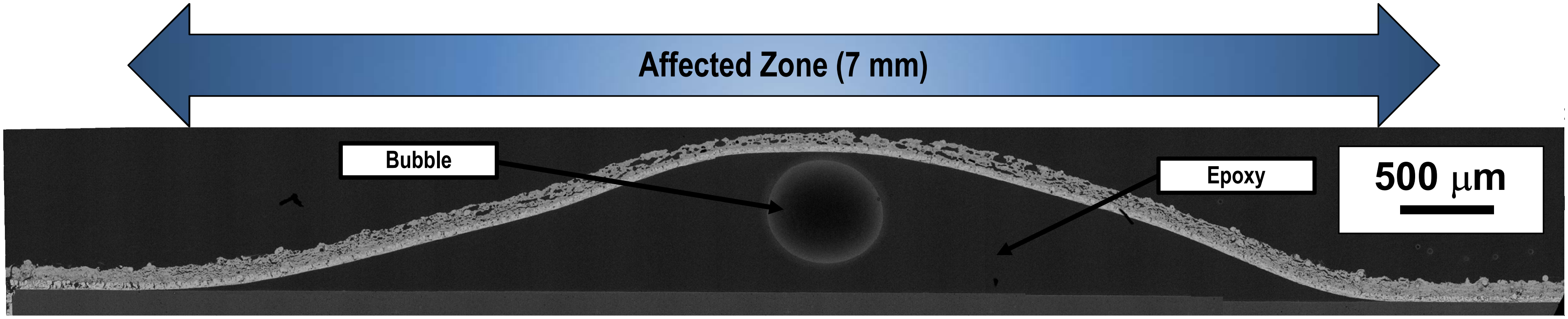
With CMAS

- Glass did not significantly attack or infiltrate the EBC
- Interaction zone with top of EBC layer of ~10μm
  - Si:Ca:Yb ratio of 3:1:1
- Underlying EBC and bond coat did not show any signs of glass infiltration

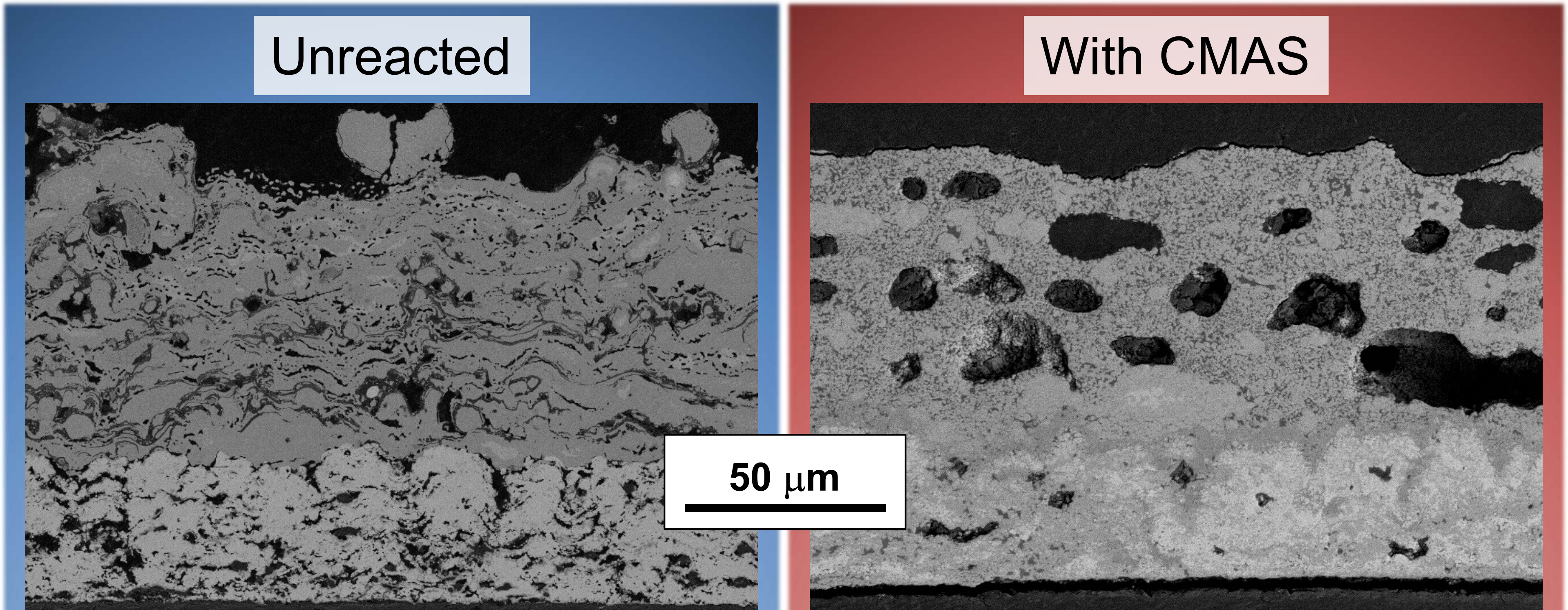
1300°C/10hr

- Tape completely wet surface and coating raised off surface by ~0.75mm
- Total 'affected zone' was ~7mm
- Macro image showed coating was thinned near the center of the tape



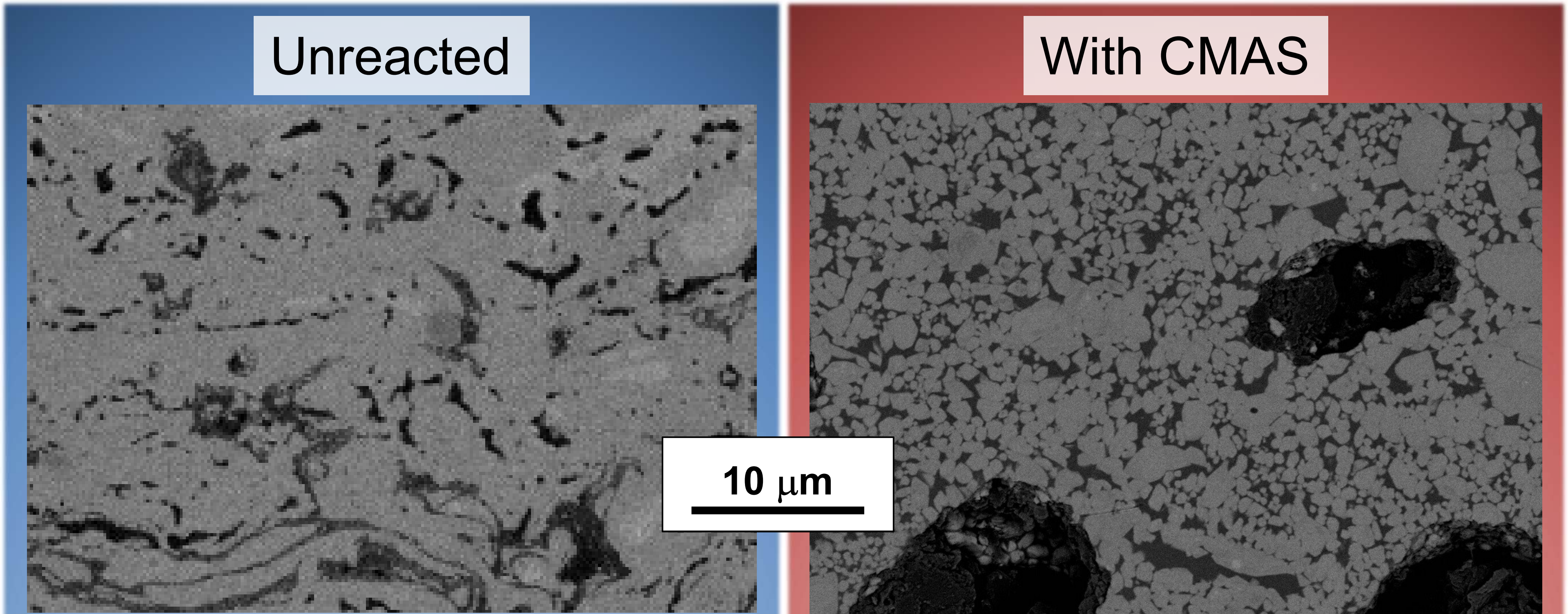


1300°C/10hr



- Glass penetrated through both the EBC and bond coat layers
  - Residual glass had similar to starting composition (Si:Ca 3:1)
- Top coat had large pores and coating material suspended in residual glass
  - Much more homogeneous, no sign of Yb_2SiO_5
- Bond coat significantly densified and HfO_2 had more rounded microstructure
  - Little or no Si/SiO_2 present after reacting with CMAS

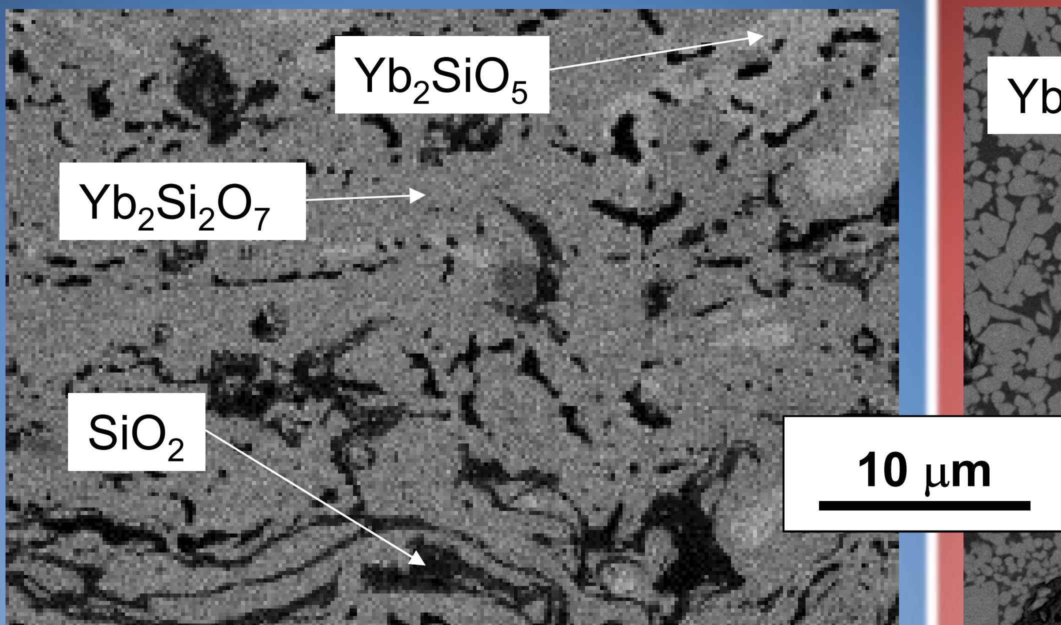
1300°C/10hr (Top Coat)



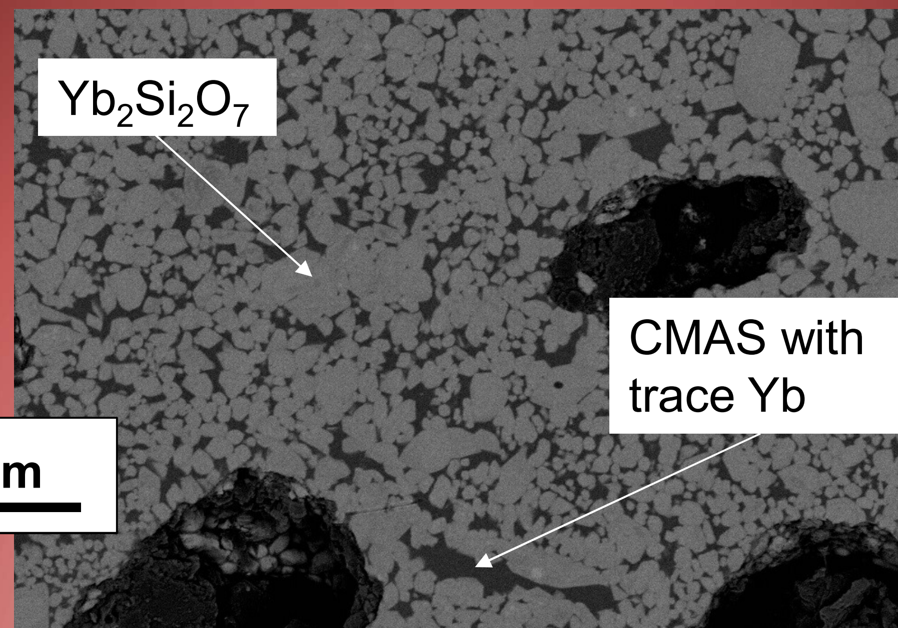
- Glass penetrated through both the EBC and bond coat layers
  - Residual glass had similar to starting composition (Si:Ca 3:1)
- Top coat had large pores and coating material suspended in residual glass
  - Much more homogeneous, no sign of Yb_2SiO_5
- Bond coat significantly densified and HfO_2 had more rounded microstructure
  - Little or no Si/SiO_2 present after reacting with CMAS

1300°C/10hr (Top Coat)

Unreacted

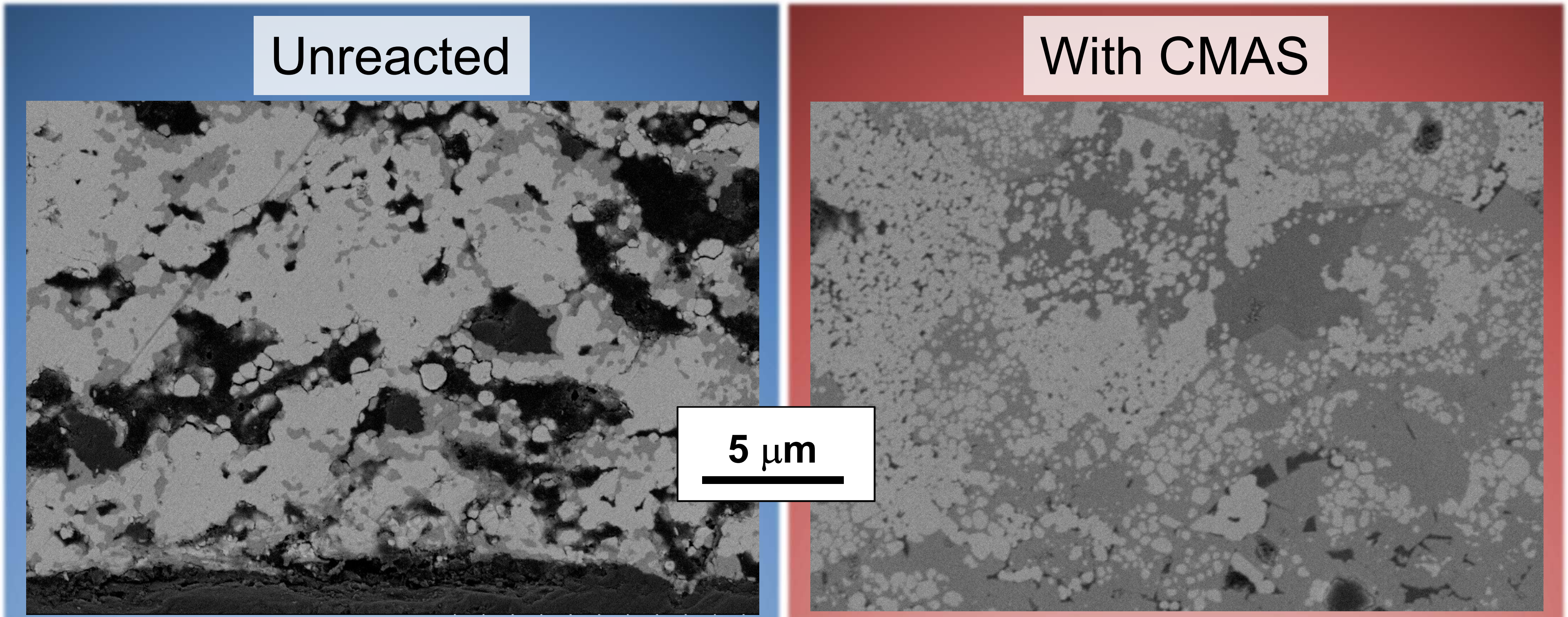


With CMAS



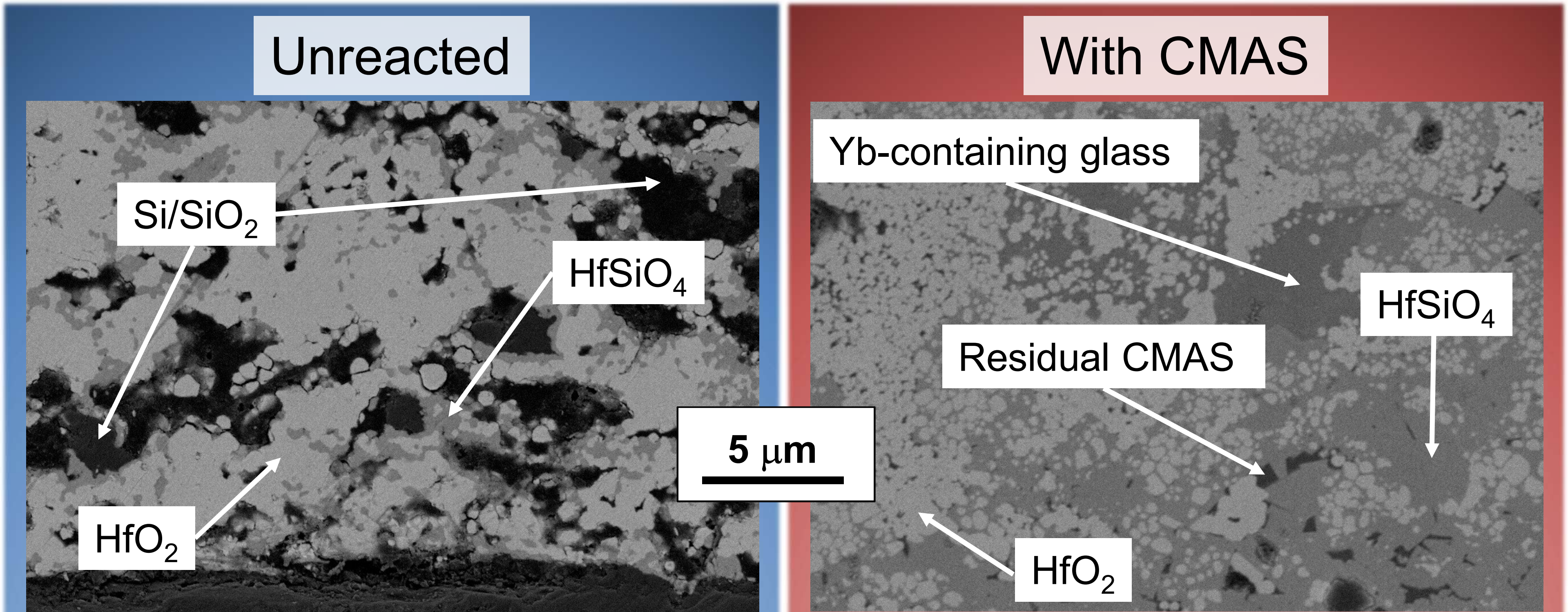
- Glass penetrated through both the EBC and bond coat layers
  - Residual glass had similar to starting composition (Si:Ca 3:1)
- Top coat had large pores and coating material suspended in residual glass
  - Much more homogeneous, no sign of Yb_2SiO_5
- Bond coat significantly densified and HfO_2 had more rounded microstructure
  - Little or no Si/SiO_2 present after reacting with CMAS

1300°C/10hr (Bond Coat)



- Glass penetrated through both the EBC and bond coat layers
  - Residual glass had similar to starting composition (Si:Ca 3:1)
- Top coat had large pores and coating material suspended in residual glass
  - Much more homogeneous, no sign of Yb_2SiO_5
- Bond coat significantly densified and HfO_2 had more rounded microstructure
  - Little or no Si/SiO_2 present after reacting with CMAS

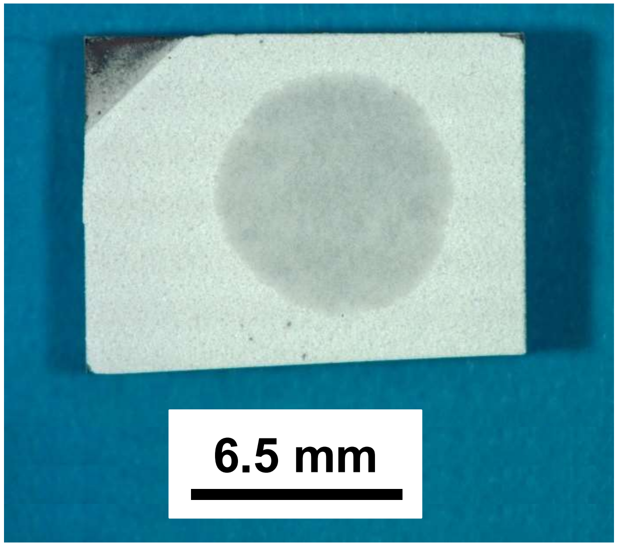
1300°C/10hr (Bond Coat)

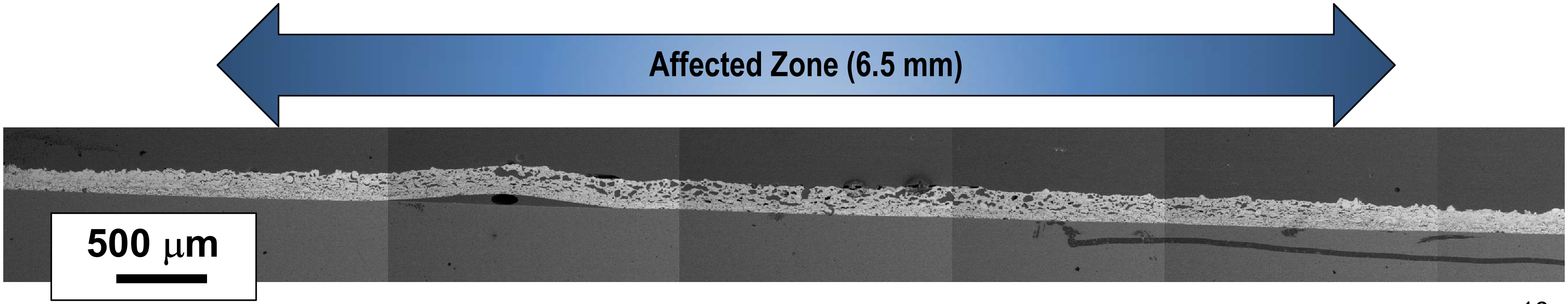


- Glass penetrated through both the EBC and bond coat layers
  - Residual glass had similar to starting composition (Si:Ca 3:1)
- Top coat had large pores and coating material suspended in residual glass
  - Much more homogeneous, no sign of Yb_2SiO_5
- Bond coat significantly densified and HfO_2 had more rounded microstructure
  - Little or no Si/SiO_2 present after reacting with CMAS

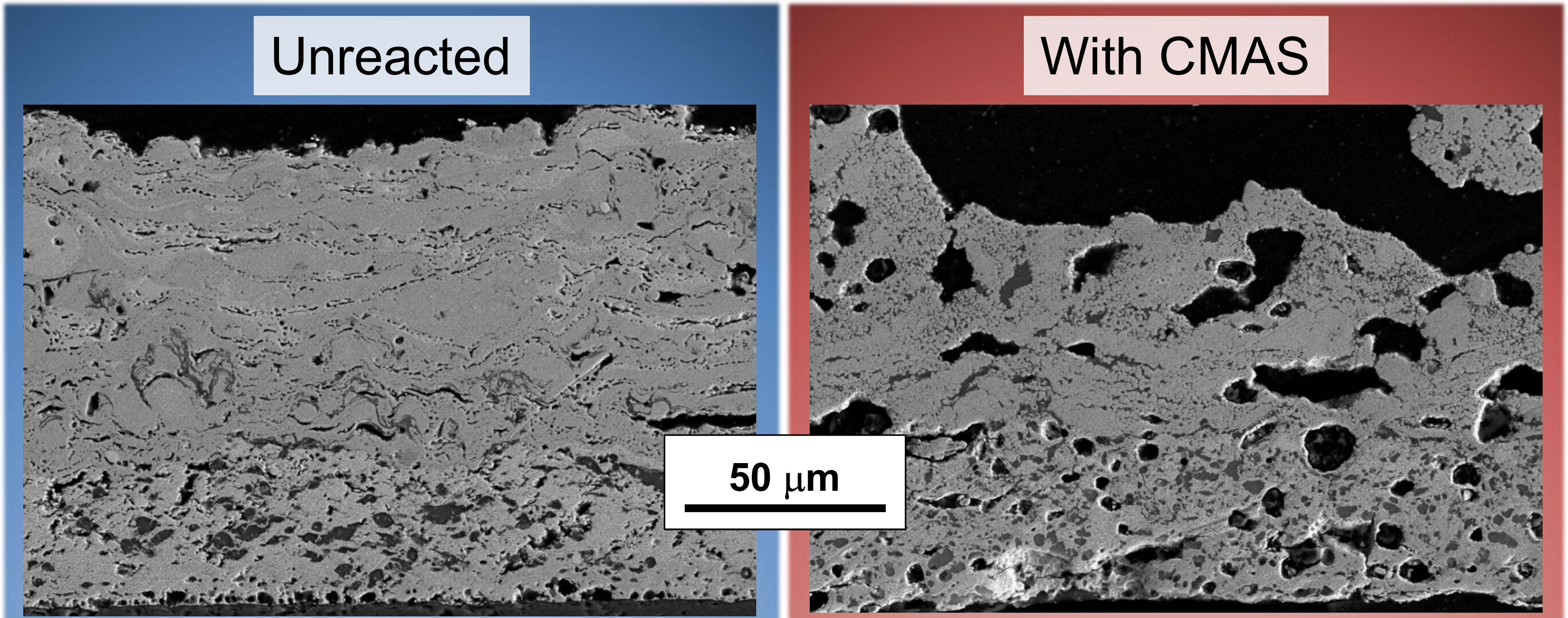
1400°C/1hr

- Tape completely wet surface and roughened surface of the coating
- Total ‘affected zone’ was ~6.5mm
- Macro image shows significant porosity in the EBC top coat



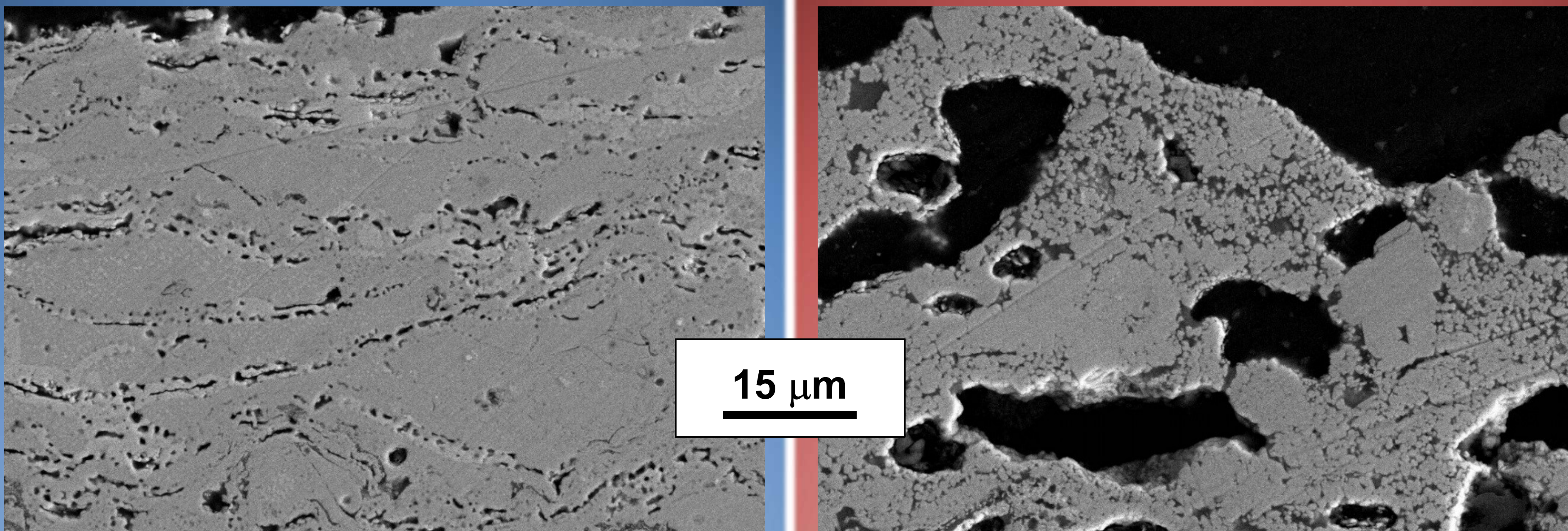


1400°C/1hr



- Even after 1 hour at 1400C, there was significant damage to the coating
- Yb-silicate topcoat was aggressively attacked, resulting in large pores within mixture of residual glass and $Yb_2Si_2O_7$
- Bond coat porosity increased significantly although evidence of CMAS presence was limited
  - Si/SiO_2 present and limited evidence of dissolution/reprecipitation

1400°C/1hr (Top Coat)

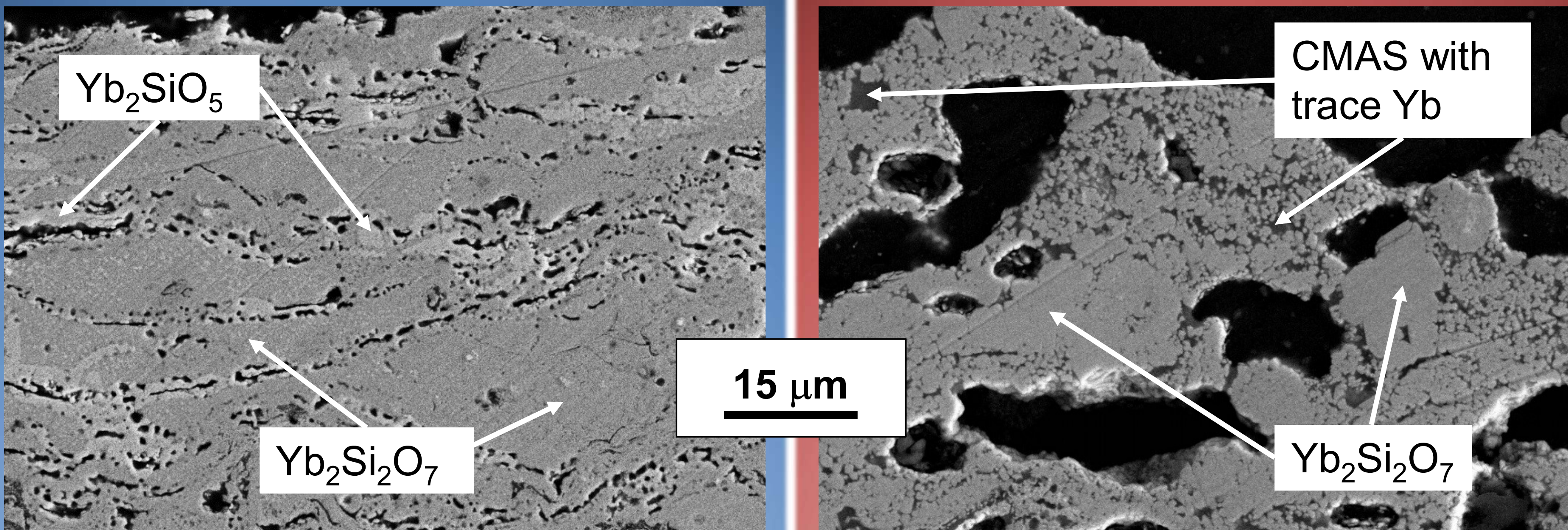


- Even after 1 hour at 1400C, there was significant damage to the coating
- Yb-silicate topcoat was aggressively attacked, resulting in large pores within mixture of residual glass and $Yb_2Si_2O_7$
- Bond coat porosity increased significantly although evidence of CMAS presence was limited
  - Si/SiO_2 present and limited evidence of dissolution/reprecipitation

1400°C/1hr (Top Coat)

Unreacted

With CMAS

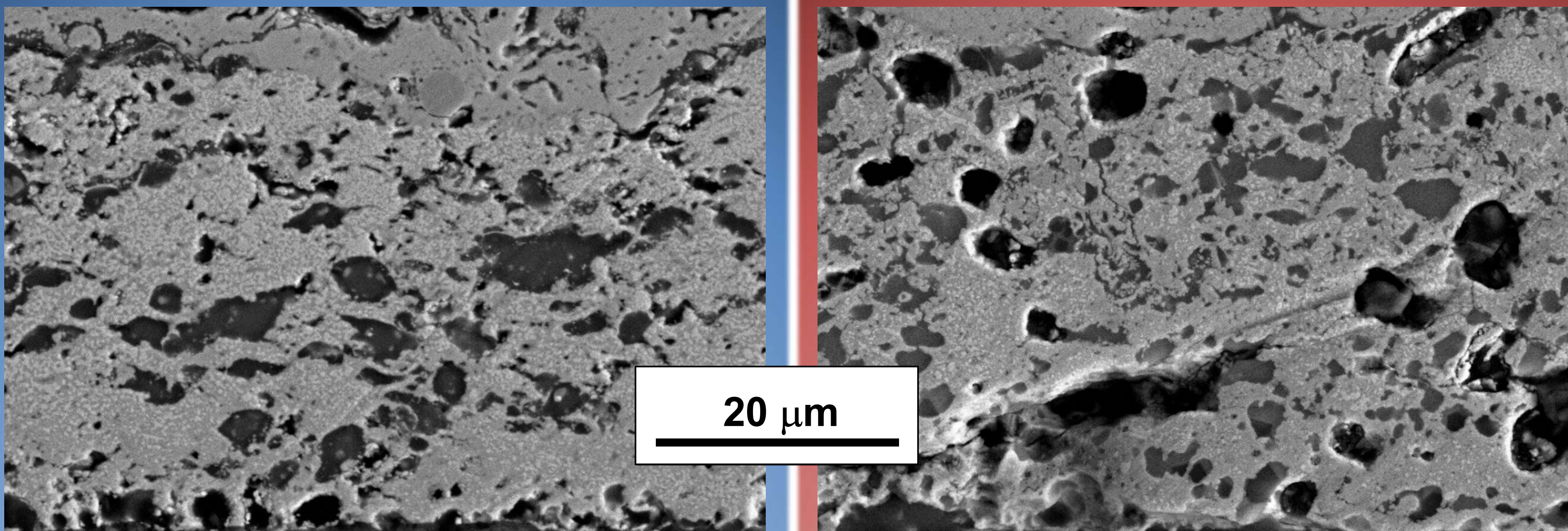


- Even after 1 hour at 1400C, there was significant damage to the coating
- Yb-silicate topcoat was aggressively attacked, resulting in large pores within mixture of residual glass and $Yb_2Si_2O_7$
- Bond coat porosity increased significantly although evidence of CMAS presence was limited
  - Si/SiO_2 present and limited evidence of dissolution/reprecipitation

1400°C/1hr (Bond Coat)

Unreacted

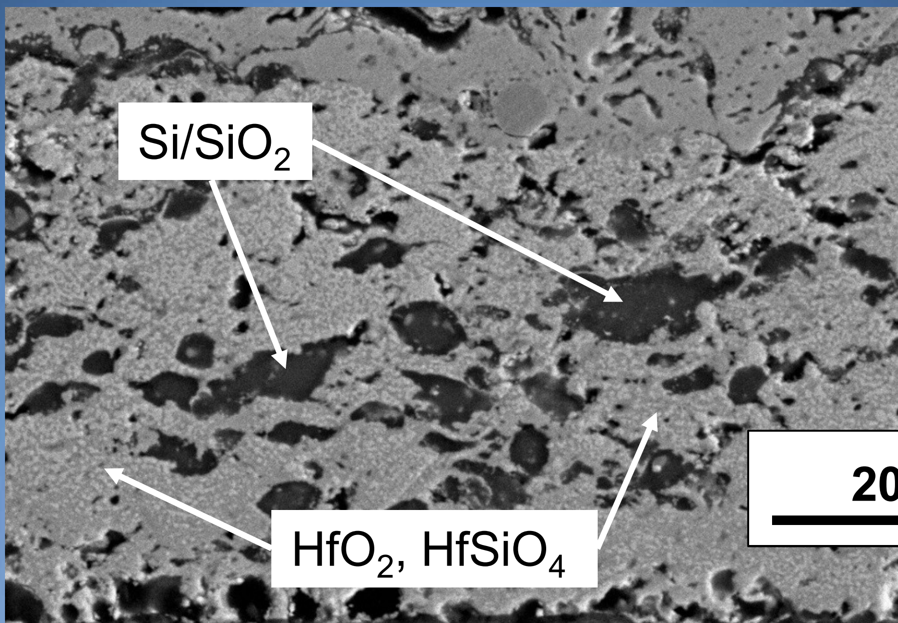
With CMAS



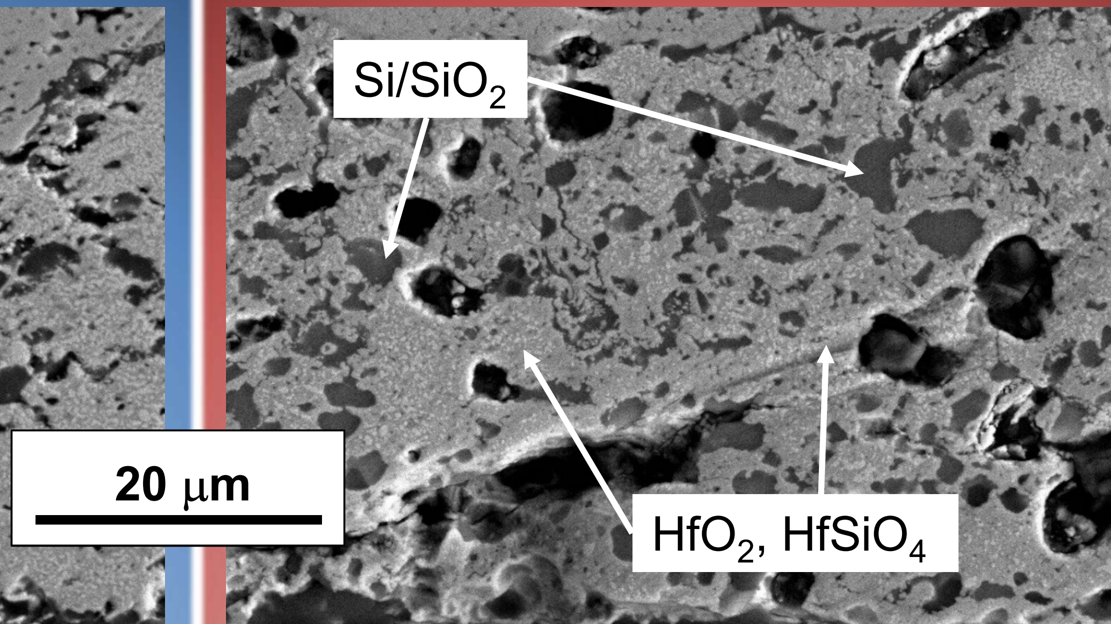
- Even after 1 hour at 1400C, there was significant damage to the coating
- Yb-silicate topcoat was aggressively attacked, resulting in large pores within mixture of residual glass and $Yb_2Si_2O_7$
- Bond coat porosity increased significantly although evidence of CMAS presence was limited
  - Si/SiO_2 present and limited evidence of dissolution/reprecipitation

1400°C/1hr (Bond Coat)

Unreacted



With CMAS

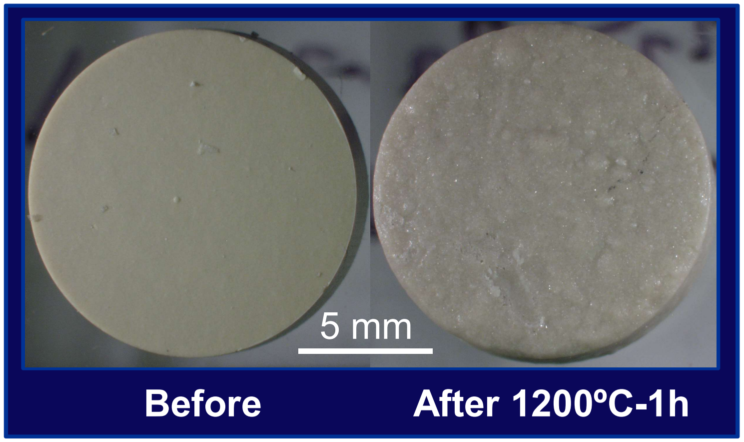


- Even after 1 hour at 1400C, there was significant damage to the coating
- Yb-silicate topcoat was aggressively attacked, resulting in large pores within mixture of residual glass and $Yb_2Si_2O_7$
- Bond coat porosity increased significantly although evidence of CMAS presence was limited
  - Si/SiO_2 present and limited evidence of dissolution/reprecipitation

Identifying Phase Development using XRD

- Heat treated powder pellets in air
  - 75/25 wt.% EBC powder ($Yb_2Si_2O_7$) with CMAS glass
  - 75/25 wt.% "Bond Coat" material ($HfSiO_4$) with CMAS glass
  - Heated in air to 1200, 1300, 1400 and 1500ºC for 50h

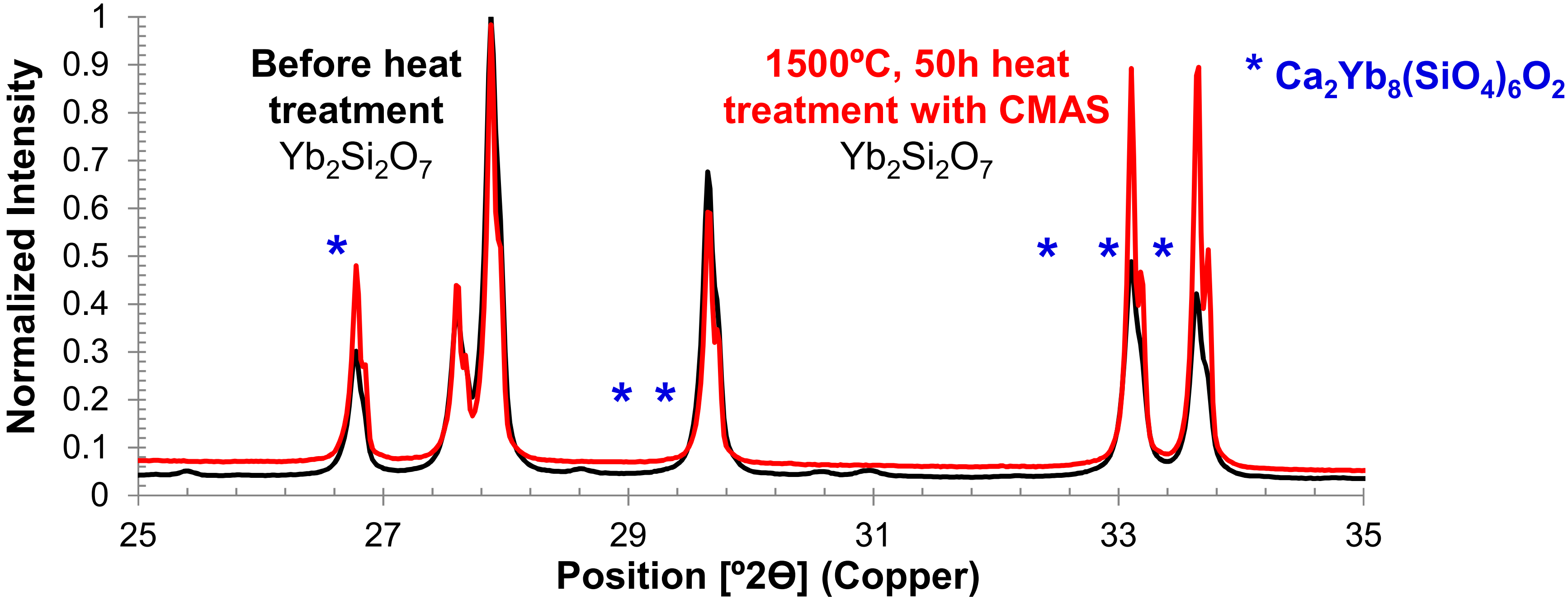
- Evaluate reacted pellet using X-ray diffraction (XRD) to compare with observed coating results



Solid State Reaction of CMAS with $Yb_2Si_2O_7$

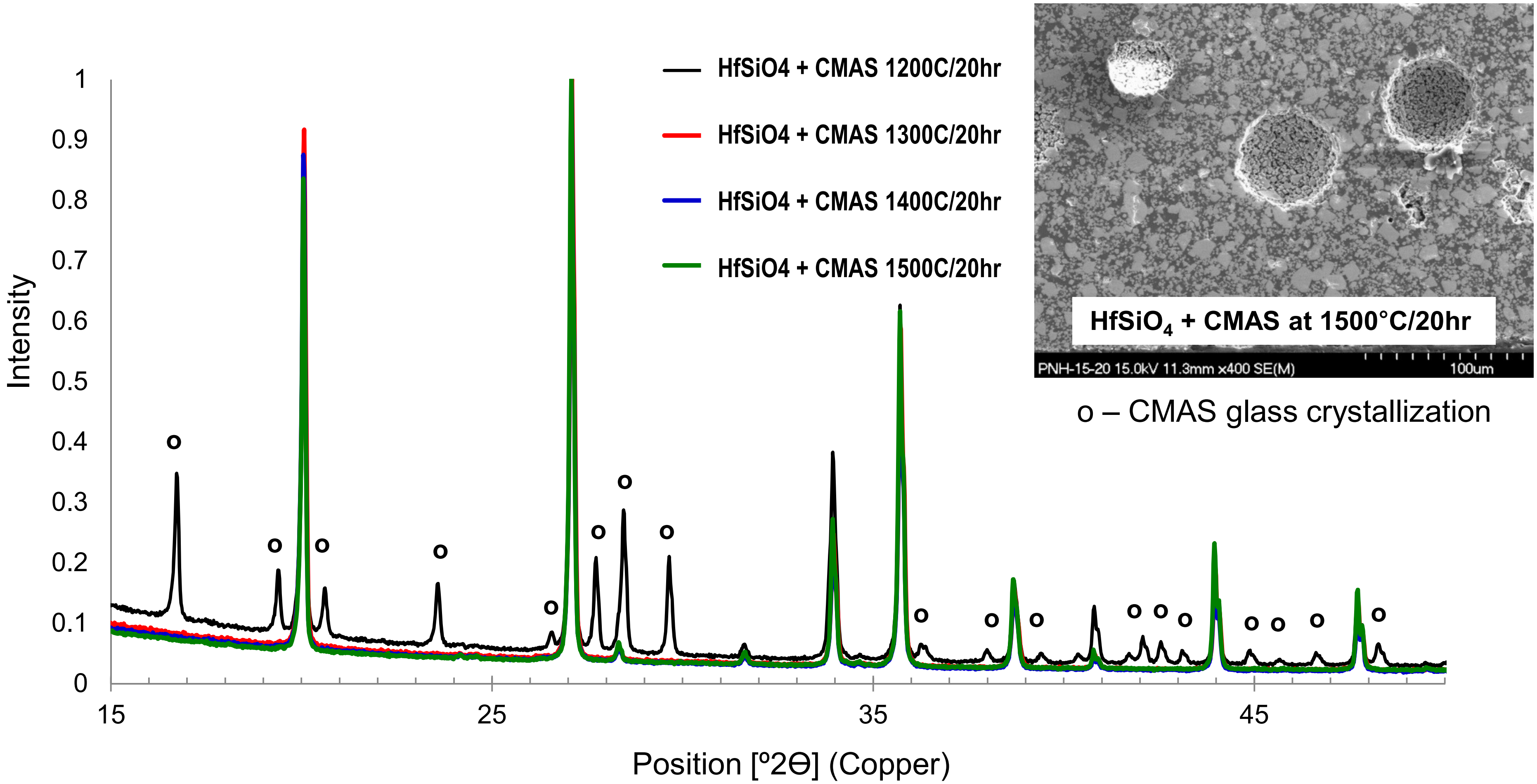
- $Ca_2Yb_8(SiO_4)_6O_2$ (silicate oxyapatite) not detected in reacted powder pellets by XRD
  - Only $Yb_2Si_2O_7$ phase detected

- Previous study[1] suggests some dissolution occurs, though not quantifiable by XRD
  - Crystalline $Yb_2Si_2O_7$ content decreased with no second phase developing



[1] F. Stolzenburg, M.T. Johnson, K.N. Lee, N.S. Jacobson, K.T. Faber, *Surface and Coatings Technology* 284 (2015) 44-50.

Solid State Reaction of CMAS to $HfSiO_4$



o – CMAS glass crystallization

Phases Detected in All Pellets

Hafnium Silicate ($HfSiO_4$)
Hafnium Oxide (HfO_2)
Silicon Oxide (SiO_2)

SEM/EDS confirms CMAS composition suggesting CMAS is amorphous glass ≥1300°C

Conclusions

- A two-layer environmental barrier coating system of Si-HfO_2 and $Yb_2Si_2O_7$ was deposited via Plasma Spray-Physical Vapor Deposition (PS-PVD) and samples were exposed to CMAS isothermally in air at a loading of 29 mg/cm^2.

- At 1200°C the attack of the EBC topcoat was limited to less than 10 microns, but the reaction layer was not an oxyapatite phase.

- Above 1200°C the CMAS composition aggressively attacked the Yb-silicate resulting in dissolution of the topcoat but no additional phases were observed.

- The Si-HfO_2 layer was infiltrated with CMAS, which reached the substrate, but the bond coat remained intact (albeit with some glass present).

- Phase analysis of heat treated mixtures of CMAS with $Yb_2Si_2O_7$ and $HfSiO_4$ provided similar results of limited secondary phases forming from reaction.

- Overall, these two-layer systems do not provide adequate protection against CMAS either from penetration or melt stabilization.

Acknowledgements

- Kang Lee
- Ed Sechkar
- Scott Panko
- Nate Jacobson
- Terry McCue
- Rick Rogers
- Joy Buehler